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A STUDY OF THE EFFECT OF SOLVENTS ON A MONOMOLECULAR REACTION

By

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A Thesis
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Introductory

As pointed out by Lewis[1], since many reactions proceed with a finite and measurable velocity it is obvious that all the molecules are not in the same chemical state at one time. If such were the case there is every reason to believe that all chemical reactions would take place instantaneously.

It is now generally recognized that in all reactions, and more especially in monomolecular reactions as will be pointed out, the velocity of the reaction is not wholly dependent upon the kinetic energy of the molecules but rather upon their internal energy. Whenever this internal energy exceeds a certain value, peculiar to the molecule undergoing change, the molecule assumes an activated condition and will react. Arrhenius[2] has assumed that in all systems an equilibrium exists between these two states in which a molecule may exist and has designated those in which the internal energy exceeds the critical value as "active" and the others as "passive". He further supposed that the number of active molecules is so small that the number of passive molecules is, for purposes of calculation, equal to the concentration of the substance.

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(1) W. C. Lewis, "Radiation, the Fundamental Factor in all Chemical Change", Scientia 25, 450 (1919)
(2) Z.physik. Chem. 4, 226 (1889)

With these assumptions Arrhenius obtained an empirical equation expressing the effect of temperature on the velocity of reaction:

$$\frac{d \ln k}{d T} = \frac{A}{T^2}$$

In this expression A is a constant for any particular reaction and denotes one-half the heat required to transform one gram-molecule of the substance from the passive to the active condition.

It is well known that the velocity of most chemical reactions increases enormously with increase in temperature, such that at ordinary temperatures it usually doubles or trebles for a 10° rise. Attempts have been made to deduce the velocity of reaction from the number of collisions which occur between the reacting molecules on the assumption that the molecules of a liquid or gas are always in a state of active motion. However O. E. Meyer[1] has shown that the increase in the number of collisions of the molecules of a gas is less than one per cent per degree rise in temperature and we can safely assume that the frequency of collision of the molecules in a dilute solution will be of the same order of magnitude. Nor will decrease in the viscosity of a liquid with rise in temperature account for the disproportionality, since generally this is no more than

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(1) Kinetische Theorie der Gase, (1877)

two per cent per degree rise in temperature.

Jean Perrin in his book "Les Atomes" has advanced the hypothesis that the action of light plays an important role in all chemical reactions. In a later paper[1] he calls attention to a peculiar relationship existing between the Arrhenius equation for reaction velocity and the Wien radiation law. Wien's law shows the natural logarithm of the intensity of any monochromatic black body radiation to be a linear function of the reciprocal of the absolute temperature. According to the equation of Arrhenius this same relationship exists between the natural logarithm of the reaction velocity and the reciprocal of the absolute temperature.

The fact, then, that the increase in reaction velocity with rising temperature is exactly the same as the rate of increase of the intensity of some particular part of the black-body radiation, affords an explanation of the disproportionality between reaction velocity and temperature. This holds, however, only when the assumption is made that chemical action depends upon the absorption of a nearly monochromatic radiation.

The work of Trautz,[2] Marcelin and Lewis[3] has brought

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(1) Ann. phys. (9) 11, 5 - 108 (1919)
(2) Z.anorg. allgem. Chem., 102, 81 - 129(1918) and 106, 149(1919)
(3) J. Chem.Soc.,111, 389, 457, 1086(1917) Phil.Mag.39, 26 (1920)

forth a definite relationship between the heat of activation of the molecules and the frequency of the monochromatic radiation necessary to activate them. Marcelin and Rice[1] from analogy with the van't Hoff isochor have identified the A of the Arrhenius equation with $\frac{Q}{R}$ where R is the gas constant and Q the energy, expressed in calories, required to activate one gram-molecule of a substance.

Thus: $$\frac{d \ln k}{d T} = \frac{Q}{RT^2}$$

If the above assumption is valid, the slope of the line obtained from this equation should be equal to that obtained from the expression representing Wien's radiation law. This is $\frac{-hv}{k}$, where h is Planck's constant, v the frequency of the monochromatic radiation and k the gas constant per molecule. Hence equating the two:

$$\frac{hv}{k} = \frac{Q}{R}$$

But $R = Nk$ where N is Avogadros number.

Therefore:

$$Q = Nhv$$

This equation is fundamental to the quantum theory and knowing Q it affords a means of determining the value of v, the frequency of light which activates the molecules undergoing

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(1) Comp. rend., 158, 407 (1914) Rep. Brit. Ass'n., 397 (1915)

reaction. The heat of activation, Q, is calculated by means of the integrated form of the Marcelin-Rice equation from the temperature coefficient of the reaction velocity.

One of the strongest arguments for the radiation hypothesis is set forth in a monomolecular reaction. The velocity of any reaction of this order is independent of the initial concentration of reacting substance and of the pressure[1]. On the other hand the number of collisions between the molecules is dependent upon both these factors. Consequently the reaction of any molecule must be independent of the collisions between molecules. The obvious conclusion then is that of Perrin; that radiation must be the agency which transforms the molecules from the passive to the active state at a measurable rate.

Langmuir[2], in a recent paper, has made calculations upon the rather meager data available in the literature, and shows that in its present state the radiation hypothesis is untenable. According to the fundamental law of Grotthus the reacting substance must absorb the radiation which causes the reaction. Therefore there should be an absorption band which includes the activating frequency. He has computed the critical frequency for the dissociation of a number of colorless gases and finds them all to lie within the visible portions

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(1) See work of Daniels and Johnston where a monomolecular reaction was followed by measuring the increase in pressure on a system. J. Am. Chem. Soc., 43, 53 - 71 (1921)
(2) J. Am. Chem. Soc., 42, 2190 - 2205 (1920)

of the spectrum where, for colorless gases, there can be no appreciable absorption.

Until the work of Daniels and Johnston[1] on nitrogen pentoxide was published in 1921, the only monomolecular gas phase reaction, not catalyzed by the vessel wall, reported in the literature was the decomposition of phosphine[2]. Making computations from this on the basis of the Perrin-Lewis theory, Langmuir shows that the total energy radiated from the vessel walls in the neighborhood of the activating wave length, 392 μμ, is far from sufficient to supply the energy required to activate the number of molecules undergoing decomposition.

Daniels and Johnston have found the heat of activation for the decomposition of nitrogen pentoxide in the gas phase to be 24,700 calories. From this value the wave length of light necessary to bring about activation is calculated to be 1.16 μ. Their experiments show, however, that light of this frequency of greater density than that emitted by thermal radiation from the vessel walls, fails to increase the rate of decomposition of the nitrogen pentoxide.[3]

Although there is undoubtedly some close relationship between radiation and chemical action, the majority of the

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(1) Loc. cit.
(2) Trautz and Bhandarkar, Z. anorg. allgem. Chem. 106, 95(1919)
(3) J. Am. Chem. Soc., 43, 73 - 81 (1921)

experimental evidence to date tends to show that in its present form the radiation hypothesis does not hold.

The activity which has recently centered about the radiation hypothesis has renewed an interest in the radiation theory for catalysis. Any foreign substance which would increase the density of the activating radiation would be a positive catalyst to the reaction. Daniels and Johnston have shown that light between 400 µµ and 460 µµ is effective in accelerating the decomposition of nitrogen pentoxide, provided however, some nitrogen peroxide is present in the system; and that the rate of decomposition is proportional to the amount of peroxide present up to a limiting concentration. Nitrogen peroxide is then a positive catalyst to the decomposition of nitrogen pentoxide in the light. Their results on a previous research however show that it is not an auto-catalyst in the dark. The authors suggest that possibly the nitrogen peroxide absorbs a considerable amount of radiation of low intensity over a wide range of blue light where it possesses an absorption band, and through fluorescence passes it out under high intensity through a very narrow range in the infra-red region where lies the activating frequency of the nitrogen pentoxide. This hypothesis requires that nitrogen peroxide be an auto-catalyst to the dark reaction, but as pointed out by the authors, the amount of energy radiated between 400 u u and 460 by a black body at the temperatures of their experiments is negligible.

To develop a simple system whereby the existing theories for the influence of radiation on chemical action could be subjected to experimental test is the purpose of this research. The ideal system for such a study is obviously a monomolecular reaction where the reacting substance is maintained in solution in suitable solvents. A monomolecular reaction is peculiarly valuable since its velocity is not influenced by such factors as molecular collision, viscosity of the reaction medium, et cetera, to which all reactions of higher order are subject. In carrying a reaction out in solution rather than in the gas phase, the experimenter is enabled to the more easily determine the effect of foreign materials upon the velocity of reaction.

Cox[1] has carried out a similar research in order to determine whether those solvents which increase the reaction velocity tend to decrease the temperature coefficient of the reaction. This is a necessary consequence of the Perrin-Lewis theory. He has studied the reaction of w-Bromoacetophenone with aniline in a number of organic solvents and also the reaction between sodium b-naphthoxide and ethyl iodide in several of the liquid alcohols. He finds the radiation theory to hold, as far as the effect on the temperature coefficient is concerned, for related solvents only. He has made no effort

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(1) J. Chem. Soc., 119, 142 - 158 (1921)

to discover a relationship between the activating frequency of his reactions and the absorption spectra of his solvents. It should also be pointed out that both his reactions are of the second order and therefore influenced, to some extent at least, by a number of factors including the kinetic energy of the molecules, the viscosity of the solvents, and in the second-named reaction by dissociation. These disturbing influences are entirely eliminated in a mono-molecular reaction as Perrin has pointed out.

Daniels and Johnston have found the decomposition of gaseous nitrogen pentoxide to be a reaction of the first order which proceeds at a measurable rate at room temperatures. This substance is fairly soluble in carbon tetrachloride and is without chemical action upon it. Furthermore, carbon tetrachloride is transparent throughout the entire visible portion of the spectrum and far into the infra-red - approximately to 12 µ. Consequently work was commenced with this solvent.

Preparation and Purification of Materials

The nitrogen pentoxide was prepared by the method described by Daniels and Bright[1] in their study of the vapor pressure of the substance. Uncombined water is removed from nitric acid by two distillations off conc. sulphuric acid and the product dehydrated with phosphorus pentoxide. The nitrogen pentoxide formed is distilled off the phosphoric acid, through phosphorus pentoxide and condensed in a U-tube surrounded by a freezing mixture, 20° below zero. A second distillation through phosphorus pentoxide in a current of ozonized air suffices to produce pure white, anhydrous crystals of nitrogen pentoxide. The ozone prevents the formation of any nitrogen peroxide.

In the early stages of the work, the nitrogen pentoxide was distilled directly from the U-tube into the solvent contained in a wash bottle. However this practice was discontinued upon examination of the literature, for according to Fischer and Tropsch[2] ozone forms unstable compounds with a number of the solvents it was desired to use. Instead, the material was distilled the second time into another smaller

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(1) Daniels and Bright, J.Am.Chem.Soc., 42, 1131 - 41 (1920)
See also: Weber, J. Prakt. Chem., 6, 342 (1873)
Berthelot, Ann. chem. phys., 6, 202 (1875)
Russ and Pokomy, Monatsh., 34, 1051 (1913)

(2) Fischer and Tropsch; Ber., 50, 765 - 7 (1917)

U-tube which was then sealed off. Preserved on ice the crystals would thus keep indefinitely.

The carbon tetrachloride used was prepared from Mallinckrodt's "technical". Sulphur was removed by allowing the liquid to stand over mercury for a week with occasional shaking. After drying with phosphorus pentoxide the carbon tetrachloride was fractionated, using a tall fractionating column. Only the middle fraction, distilling over through a range of .03°, was used in the experiments.

Experimental

The apparatus in its final form is shown in Figure 0. The decomposition bulb is of 100 cc. capacity, similar to those used by Walton[1] and his students in their researches on hydrogen peroxide, but so modified as to reduce all rubber connections to a minimum. Rubber is very readily attacked by both nitrogen pentoxide and nitrogen peroxide, one of the products of the reaction. The bulb was connected by capillary tubing, some eighteen inches in length, to a 100 cc. burette, water-jacketed so as to prevent irregularities of the burette readings due to changes in temperature of the gas enclosed in the burette. On the experiments at 25° and 35° water from the thermostat was pumped through the water-jackets but at the higher temperatures, the circulation was provided through a separate, hand-controlled thermostat maintained near the room temperature. The gas was measured over the solvent being used in the experiment, previously saturated with oxygen.

The reaction was assumed to take place the same as in the gas phase in accordance with the following equation:

$$\begin{array}{cccc} 2\,N_2O_5 & \rightleftarrows & 2\,N_2O_4 & +\ O_2 \\ & & \uparrow\downarrow & \\ & & 4\,NO_2 & \end{array}$$

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(1) Walton and Judd: Zeit. phys. chem., 83, 315 (1913)

Most of the nitrogen peroxide formed remained dissolved in the carbon tetrachloride. However some always passed into the vapor state and tended to pass over into the burette and render the readings erroneous. To prevent this six inches of one-half inch glass tubing, filled with glass wool wet with conc. sulphuric acid and water-jacketed,were interposed between the burette and the decomposition chamber. In the early stages of the work, silica gel was used to accomplish this purpose but this was later abandoned when it was discovered that the above reaction could be reversed on the surface of the silica gel. This phenomenon is rather interesting from the standpoint of catalysis since it represents the reversal of an ordinarily irreversible reaction under the highly concentrated conditions existing on a surface.

The outside of the entire decomposition bulb was painted with several coats of black shellac as the reaction is sensitive to light. It was so carried in a rocking cradle, actuated rapidly by an electric motor, as to be immersed in a large water thermostat kept at the required temperature within 0.02^{o} as read on a thermometer checked against one calibrated by the Bureau of Standards.

The greatest difficulty was experienced with the indispensable rubber connection between the decomposition chamber and the capillary tubing which carried the oxygen over into the burette. Many experiments were spoiled by the development of a

leak in this connection due to the combined action of the shaking and the gases upon it. Of all forms, pressure tubing functioned the worst. The problem was ultimately solved by inserting one length of red rubber tubing inside another just large enough to take it with a very thin layer of vaseline between the two. An eight-inch length of capillary tubing was fused to the decomposition bulb so the connection was made at some distance from the bulb and at the axis of rotation of the rocking cradle as shown in Figure O.

The whole apparatus was set up in duplicate so that two determinations could be carried out at a time.

In carrying out a determination all connections between the decomposition chambers and the burettes were made gas tight and the cradle raised so as to elevate the side necks on the chambers out of the thermostat water. Twenty-five cc. of the solution of nitrogen pentoxide in the solvent were pipetted into the chambers, the glass stoppers replaced, the cradle lowered and set in motion. Care had to be observed to carefully regulate the concentration of the solution so that the total evolution of oxygen would be no greater than the capacity of the burette. This was done by titration with standard NaOH solution.

The reaction was followed in a simple manner. As the decomposition proceeded, oxygen was forced over into the burette

and the quantity read off at definite intervals. The pressure in the burette was maintained at atmospheric pressure by removing the burette liquid as it rose in the side-arm. All readings were corrected to 0^o and 760 mm. pressure. Time readings were taken on a stop watch. The final observation was made when no further increase in volume was noticed after a long period of time (sometimes overnight).

The initial evolution of gas was always very abnormal and was proportional to the age of the solution. This was due to the disruption of a supersaturation of oxygen in the solution when the shaking was commenced. In every case some decomposition of the nitrogen pentoxide in the solution occured before use and the oxygen resulting from this, instead of being evolved, produced a condition of supersaturation in the solution which was usually considerable. Results given below in this paper show strikingly the effect of shaking upon this condition of supersaturation. For this reason the initial readings have in most cases been omitted in the calculations of the reaction- velocity constants.

The early experiments were all carried out with smaller decomposition chambers completely filled with solution, so that with the measuring burettes wholly filled with carbon tetrachloride or other liquid, there existed practically no free space above the solution. This obviated the possibility

of any nitrogen pentoxide decomposing in the gas phase at the start of the reaction. However no change in the reaction velocity could be detected in the latter stages of an experiment when some nitrogen pentoxide undoubtedly did exist in the free space above the liquid in the partially emptied burettes. This, together with the fact that bubbles of oxygen were actually evolved from the solution, was taken as proof that any decomposition occurring in the gas phase was not influencing the results.

Figure 1 shows the actual burette readings reduced to standard conditions plotted against time in seconds as abscissa. The curves cannot be compared directly with one another since the total oxygen evolved varied with each experiment. This fact is well illustrated by comparing the two sets of curves obtained in four experiments at 45°: Nos. 53 and 54; 55 and 57.

Experiments were not made above 55° for in doing so accuracy would be sacrificed for speed in observation and because the reaction would be completed before the shaking process had completely broken up the supersaturation previously mentioned. Furthermore, nothing was done below 25° because of the long time involved in the completion of an experiment at those temperatures.

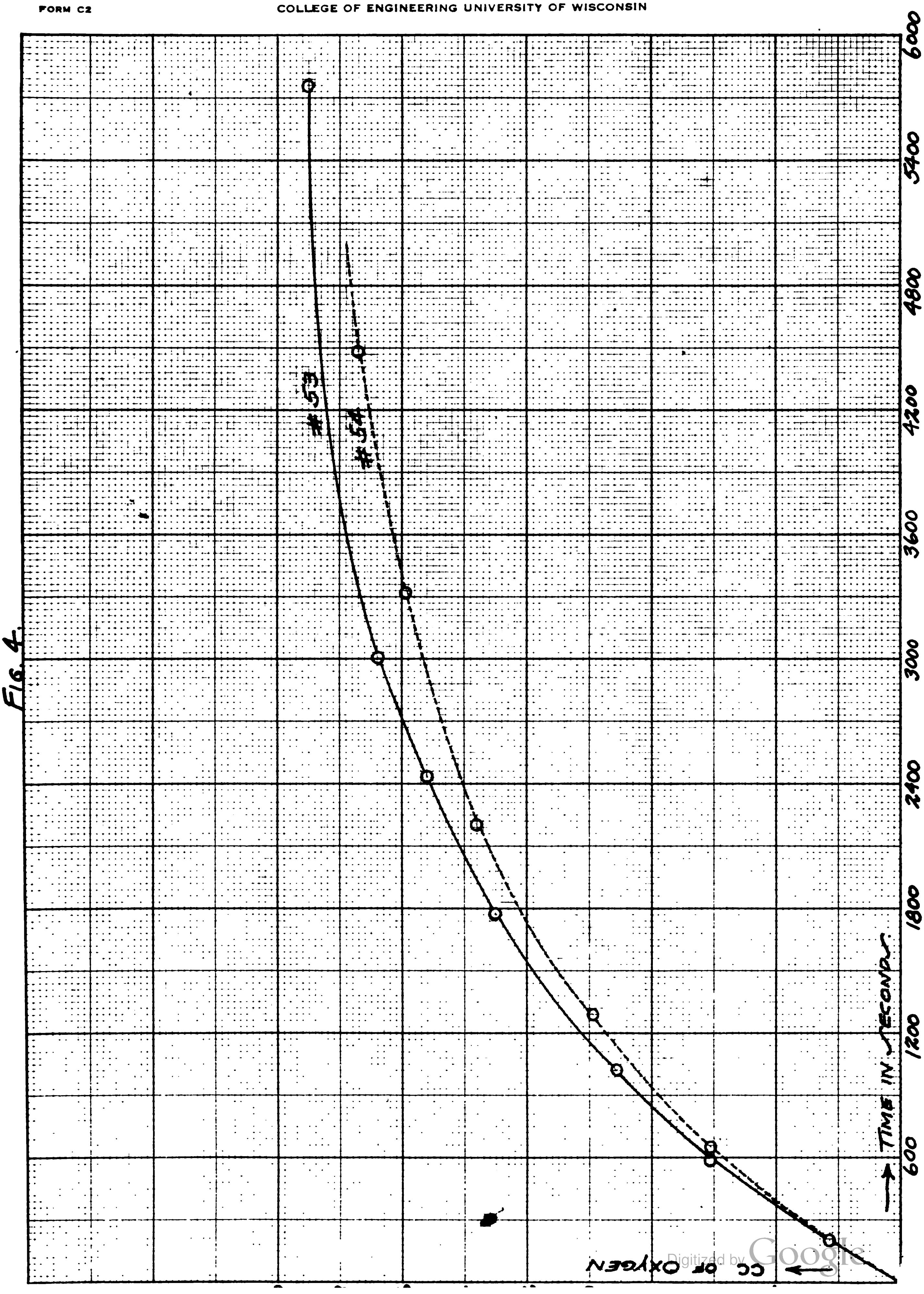

FIG. 4.

#53
#54
600
1200
1800
2400
3000
3600
4200
4800
5400
6000
→ TIME IN SECONDS
← CC OF OXYGEN

Table IV - 45°

No. 55($V_0 = 12.82$)($V_\infty = 53$)				No. 57($V_0 = 12.86$)($V_\infty = 55$)		
t	$V_t - V_0$	$V_\infty - V_t$	$k \times 10^{-4}$	$V_t - V_0$	$V_\infty - V_t$	$k \times 10^{-4}$
0	0	40.18	----	0	42.14	----
300	6.75	33.43	----	8.00	34.14	----
600	12.20	27.98	5.93	13.59	28.55	5.96
900	16.65	23.53	5.76	18.40	23.74	6.14
1200	20.35	19.83	5.70	22.30	19.84	5.97
1500	23.55	16.63	5.85	25.75	16.39	6.35
1800	26.25	13.93	5.90	28.35	13.79	5.75
2100	28.50	11.68	5.87	30.50	11.64	5.65
2700	32.10	8.08	6.13	34.00	8.14	5.95
3300	34.70	5.48	6.48	36.25	5.89	----
3900	36.60	3.58	----	------		
∞	40.18	0	----	42.14		----
		Avg.	5.95		Avg.	5.97

FIG 2.

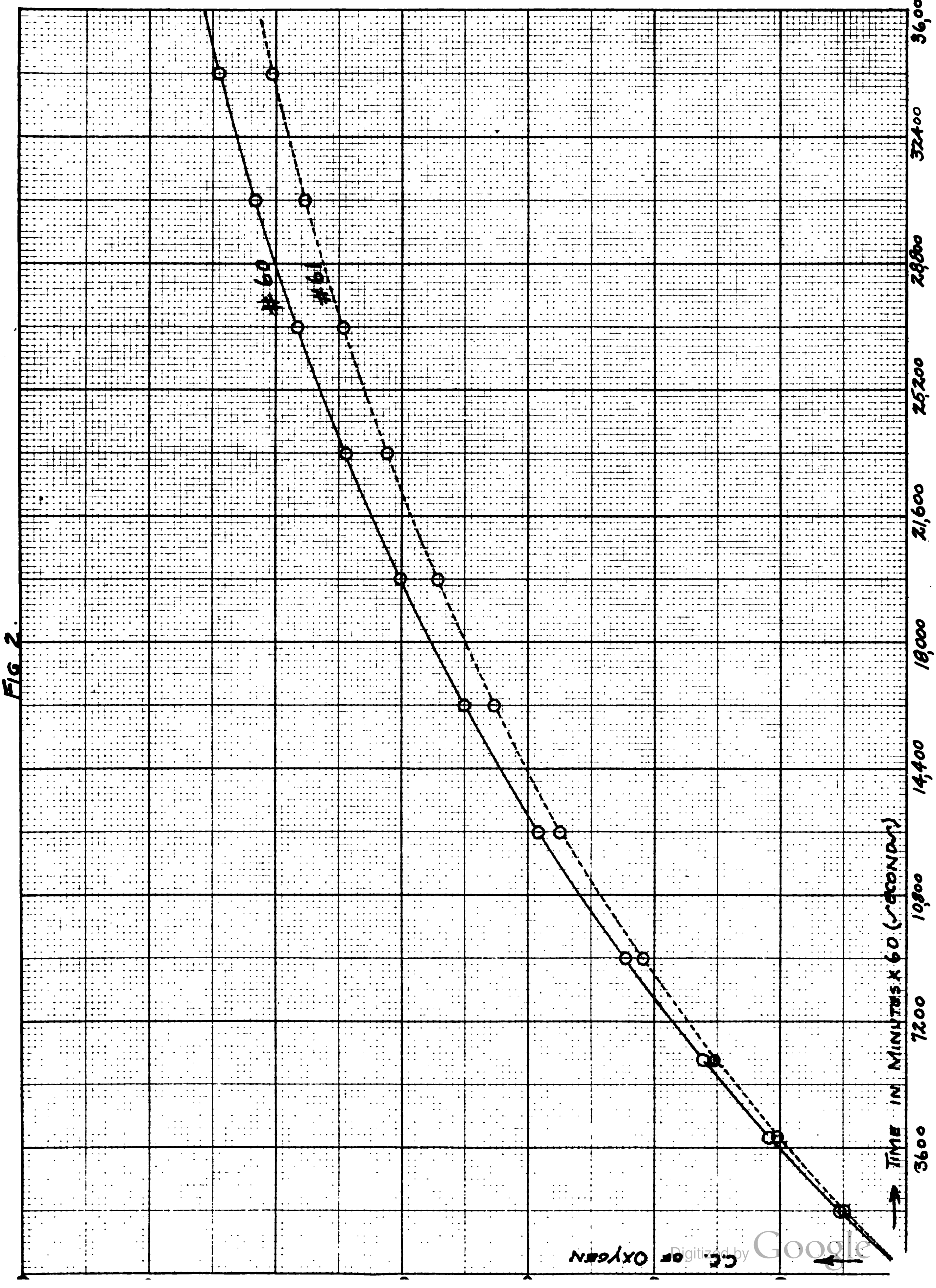
#60
#61
3600
7200
10800
14,400
18,000
21,600
25,200
28,800
32,400
36,000
→ TIME IN MINUTES x 60 (=SECONDS)
C.C. OF OXYGEN

Table V - 55°

No. 51 ($V_o = 20.2$)($V_\infty = 43.57$)				No. 52 ($V_o = 21.2$)($V_\infty = 45.7$)		
t	$V_t - V_o$	$V_\infty - V_t$	$k \times 10^{-4}$	$V_t - V_o$	$V_\infty - V_t$	$k \times 10^{-4}$
0	0	23.37	----	0	24.5	----
60	3.35	20.02	----	3.95	20.55	----
120	6.1	17.27	22.6	6.85	17.65	----
180	8.2	15.17	21.6	9.1	15.4	22.7
240	10.05	13.32	21.7	10.95	13.55	21.3
300	11.60	11.77	20.6	12.55	11.95	21.0
360	12.95	10.42	20.3	14.00	10.5	21.6
480	15.20	8.17	20.3	16.35	8.15	21.1
660	17.75	5.62	20.8	18.80	5.7	19.9
1020	21.00	2.37	----	21.2	3.3	----
∞	23.37	----	----	24.5	0	----
		Avg.	21.1			21.3

Discussion of Results

Table VI, Ex. No. 29 presents results obtained at 55° without shaking the decomposition chamber. It will be noticed that the constant is considerably lower and shows more fluctuations than similar data obtained with shaking and given in Table V. Data obtained without shaking at the lower temperatures show a proportionately lower velocity constant and only in rare cases could consistent results be obtained without shaking. The reason for this is attributed to the formation of supersaturated solutions of oxygen in the solvent when the bulb was not shaken. Bohnson[1] has experienced similar difficulties in his work on hydrogen peroxide in this laboratory and lays it to the same phenomenon.

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(1) Bohnson. J. Phys. Chem. 24 - 677 - 700 (1920)

Table VI - 55°

Comparing results obtained in carbon tetrachloride solution without shaking with those obtained by Daniels and Johnston in the gas phase.

No. 29 ($V_0 = 0$)($V_\infty = 109.2$)				No. 26 ($p_1 = 331.3$)				
$t_2 - t$	$V_t - V_0$	$V_\infty - V_t$	$k \times 10^{-4}$	t	p	$p - p_1$	p	$k \times 10^{-4}$
57	5	104.2	----	3	424.5	93.2	72.9	----
33	10	99.2	14.8	4	449.0	117.7	95.0	14.7
67	20	89.2	15.9	5	471.5	140.2	115.9	15.4
22	25	84.2	26.7	6	491.8	160.5	135.2	15.7
--	35	74.2	----	7	509.0	177.7	151.9	14.8
42	40	69.2	16.6	8	524.8	193.5	168.0	15.7
47	45	64.2	15.9	9	539.8	207.7	182.8	15.8
47	50	59.2	17.9	10	551.3	220.0	195.7	15.1
57	55	54.2	15.4	12	572.2	240.9	217.8	14.8
61	60	49.2	15.9	14	589.4	258.1	236.4	14.9
65	65	44.2	16.5	16	604.0	272.7	252.2	15.2
80	70	39.2	15.0	18	616.3	285.0	265.9	15.8
89	75	34.2	15.3	22	634.0	302.7	285.7	15.0
105	80	29.2	15.1	26	646.0	314.7	299.3	14.8
120	85	24.2	15.7	30	654.5	323.2	309.0	15.1
158	90	19.2	14.6	38	664.2	332.9	320	14.2
202	95	14.2	14.9	∞	673.7		331.3	
∞	109.2	0	----					

In Table VI is also printed Ex. No. 26 performed by Daniels and Johnston in the gas phase. The fact that the results obtained without shaking in this research so closely approximate their results at the same temperature seems to hold a peculiar significance. A corresponding agreement existed at the lower temperatures. As previously mentioned this reaction has been reversed slowly on the surface of silica gel. It seems entirely possible that under the influence of the extraordinarily high concentration of oxygen in the supersaturated solutions the reaction was likewise reversed at a definite rate. Of course, the reverse reaction, being bimolecular, should increase in speed as the concentration of nitrogen peroxide is built up in the solution by the decomposition reaction. However, the concentration of the nitrogen peroxide is at all times, even at (V_0), so much greater than the concentration of oxygen, due to the difference of the solubility of the two in carbon tetrachloride, that any increase in its concentration can be neglected.

These observations indicate that the close proximity that maintains between oxygen and nitrogen peroxide, either in the gas phase or in the carbon tetrachloride solution supersaturated with oxygen, is a disturbing influence on the forward reaction. This connects up well with the fact that, working under very low initial pressures, Daniels and Johnston obtained values nearly equal to those obtained in this research with shaking. Further

experimentation in the gas phase will be necessary to determine the exact nature of this effect.

Several reactions reported in the literature as monomolecular are not truly such but are the results of diffusion and catalytic action of the walls of the containing vessel as indicated by their low temperature coefficients. The high temperature coefficient of this reaction, between 300% and 400% for a 10° rise, shows that this reaction is not one of this type. To further substantiate this, experiments were carried out in duplicate, one in an empty chamber and the other in one loosely packed with glass wool. The results are given in Table VII and show no striking differences despite the greatly increased surface of glass in the one.

Table VII - 55°

Showing that the reaction is not catalyzed by the vessel walls.

Empty Chamber				Chamber filled with Glass Wool			
No. 29 ($V_o = 0$)($V_\infty = 109.2$)				No. 33 ($V_o = 10$)($V_\infty = 85.2$)			
$t_2 - t_1$	$V_t - V_o$	$V_\infty - V_t$	$k \times 10^{-4}$	$t_2 - t_1$	$V_t - V_o$	$V_\infty - V_t$	$k \times 10^{-4}$
57	5	104.2	--	62	15	70.2	---
33	10	99.2	14.8	54	20	65.2	---
67	20	89.2	15.9	52	25	60.2	15.3
22	25	84.2	26.7	54	30	55.2	16.1
--	35	74.2	----	63	35	50.2	15.2
42	40	69.2	16.6	66	40	45.2	15.9
47	45	64.2	15.9	72	45	40.2	16.2
47	50	59.2	17.9	84	50	35.2	15.8
57	55	54.2	15.4	96	55	30.2	15.9
61	60	49.2	15.9	117	60	25.2	15.5
				143	65	20.2	15.5
65	65	44.2	16.5	186	70	15.2	15.3
80	70	39.2	15.0	286	75	10.2	----
	109.2	0	----		85.6	0	----
		Avg.	17.06			Avg.	15.67

The results presented in this table were obtained without shaking which accounts for the subnormal values. Experiments carried out in chambers filled with glass wool always gave more consistent results than those in empty chambers because of the tendency of the glass wool to break up supersaturation.

As previously mentioned the work of Cox on the radiation theory was an effort to determine if those substances which increased the speed of the reaction tended to decrease the temperature coefficient in accordance with the theory. Lewis[1] has come to the conclusion from an application of the Wien law to the Marcelin-Rice equation that any agency which increases the reaction velocity decreases the temperature coefficient. Skrabal[2] has arrived at the more general conclusion that the "relations between reaction velocity, temperature effects, influence of solvent, added catalyst and photochemical action are all essentially the same; accordingly, change in the reaction velocity affected by any one of these factors diminishes as the magnitude of the velocity constant increases." In this connection, Table VIII is of considerable interest.

Table VIII Temperature Coefficient of the Reaction

Temp. °C.	k	Temp. Coeff.	Mean Temp. °C.
55	.00212		
		3.47	50
45	.000611		
		3.77	40
35	.000162		
		3.96	30
25	.0000409		

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(1) Lewis, J. Chem. Soc. 109, 796 (1916)
(2) Skrabal, Monatsh. 37, 495 (1916)

It shows that as the velocity constant is increased by the agency of temperature that there is a gradual decrease in the temperature coefficient of the reaction velocity in accordance with the Perrin-Lewis theory.

The velocity constants are regular and are indicative of a monomolecular reaction, Certain fluctuations which do occur are erratic and can be traced to irregularities in the curves or to errors in reading the burettes where the volume change was very small.

Table IX - 55°

No. 51 (V_0 = 20.2) (V_∞ = 43.57)

t	$V_t - V_0$	$V_\infty - V_t$	unimolecular $k \times 10^{-4}$	bimolecular $k \times 10^{-4}$
0	-0	23.37	-----	----
60	3.35	20.02	----	-----
120	6.1	17.27	22.6	1.33
180	8.2	15.17	21.6	1.34
240	10.05	13.32	21.7	1.53
300	11.60	11.77	20.6	1.65
360	12.95	10.42	20.3	1.84
480	15.20	8.17	20.3	2.20
660	17.75	5.62	20.8	3.08
1020	21.00	2.37	----	----
	23.37	-----	----	----

In Table IX, in order to show that the reaction is not bimolecular, the velocity constants for one of the experiments (No. 51) are compared with those calculated for a bimolecular reaction with the help of the formula:

$$k = \frac{1}{t_2 - t_1} \times \frac{V_{t_2} - V_{t_1}}{(V_\infty - V_{t_1})(V_\infty - V_{t_2})}$$

where t_2 and t_1 are taken as successive time intervals as before.

Further the velocity of any monomolecular reaction is independent of the initial concentration of reacting substance. A comparison of Tables III and IV shows that this principle holds true for this reaction. Table III presents data where the initial concentration was very small while in the experiments represented by Table IV this concentration was much larger; yet there is no striking difference between the velocity constants obtained in the four experiments.

Table X is of considerable interest. It is a comparison of the values of the "critical increment" for the decomposition of nitrogen pentoxide when the reaction is taking place under two extremes of condition. The critical increment or the amount of excess energy which a molecule must accumulate before it will react is the equivalent of the "heat of activation" of the Marcelin-Rice equation. It is obtained by

substituting the appropriate values in the integrated form of this equation, giving the value for the "critical increment" in calories per gram-molecule.

$$Q = \frac{1.98\, T_1\, T_2 \times 2.302 \log_{10} k_2 \div k_1}{T_2 - T_1}$$

Table X - Calculation of the Critical Increment

Temp. °C.	k		Critical Increment		Mean Temp. °C.
	In CCl_4	Gas Phase	In CCl_4	Gas Phase	
55	.00211				
55	.00213				
Avg.	.00212	.00150	25,740	22,750	50
45	.000637				
45	.000613				
45	.000595				
45	.000597				
Avg.	.000611	.000498	25,760	25,340	40
35	.000162				
35	.000162				
Avg.	.000162	.000135	25,030	25,200	30
25	.0000421				
25	.0000398				
Avg.	.0000409	.0000338			
		Avg.	25,510		

These calculations show that over the range of temperature indicated the value of E is practically constant with a greater degree of accuracy even than was obtained in the gas phase. Obviously such a system possesses untold value for the work in hand for it is to be expected that in other solvents and in the presence of foreign materials, unacted upon chemically by the nitrogen pentoxide, equally consistent results can be obtained.

The table also shows strikingly how little influence molecular collision has on a monomolecular reaction. As far as can be learned no one reaction has been carried out under such a diversity of conditions that has yielded results agreeing so closely. The majority of the work in the gas phase was carried out under a pressure of less than one atmosphere. Taking Ex. No. 60 as an example where the total O_2 liberated was 71.2 cc., the decomposition equation shows that this is equivalent to sufficient gaseous pentoxide to occupy a volume of 142.4 cc. under standard conditions. Since this amount of nitrogen pentoxide was present in 25 cc. of solution it means that 142 cc. of gaseous nitrogen pentoxide have been forced into a volume of 25 cc. with a concomitant packing together of the molecules and a much greater frequency of collision than existed in the gas phase experiments carried out in a vacuum. Yet neither the velocity constants nor the "heat of

activation" differ proportionately from the corresponding values obtained in the gas phase.

That such conditions do not hold for all solvents has been shown in some preliminary experiments with chloroform and heptane. In chloroform the reaction proceeds much more rapidly. Further work with a number of solvents will, it is hoped, throw light on the exact factors which influence the rate of decomposition.

Dr. S. Dushman, in a recently published article,[1] has developed a theory for unimolecular reactions based upon the quantum theory in which the velocity constant is given by the relation:

$$k = \frac{Q}{Nh} \cdot e^{\frac{-Q}{RT}}$$

where Q denotes the heat of activation, h the quantum constant, N Avogadro's number and R the gas constant. For purposes of calculation this equation can be written

$$\log k = 10.0203 + \log Q - Q/4.571\ T$$

Although Dushman "lays no claim to strict validity" for this equation he has applied it to the decomposition of phosphine previously referred to and to several homogeneous gas reactions and finds that it yields satisfactory agreement with

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(1) J. Am. Chem. Soc. 43, 397 - 433 (1921)

the experimental data in a number of cases where the reactions were not catalyzed by the vessel walls. He therefore points out that it probably represents an ideal condition which would hold true in all cases but for the presence of certain unknown disturbing factors.

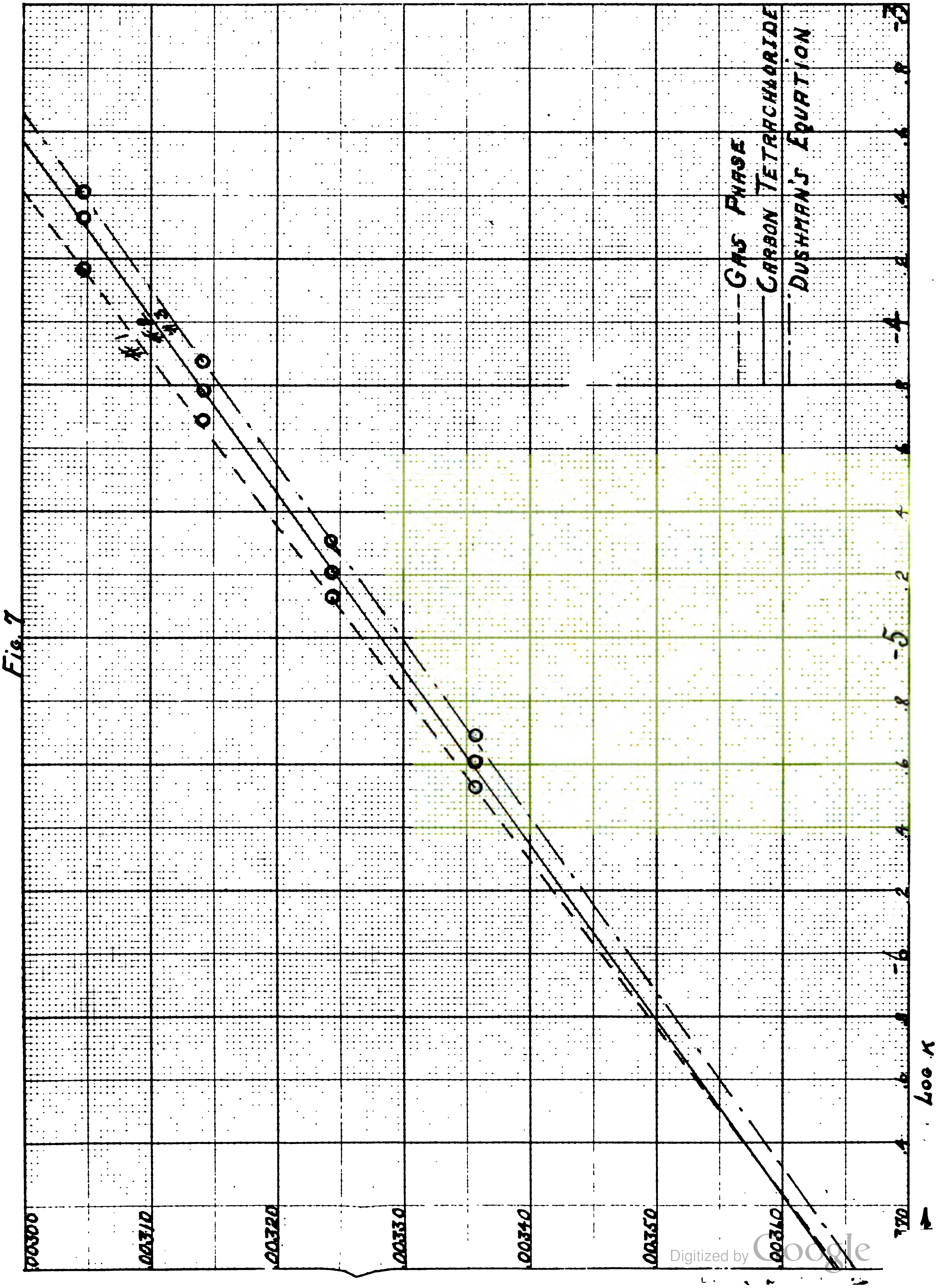
Although Dr. Dushman has applied this equation with indifferent success to rates of reactions in solutions, the decomposition of nitrogen pentoxide in carbon tetrachloride solution, being a strictly monomolecular reaction uncatalyzed by the vessel walls, affords a valuable opportunity for testing the validity of this expression.

Table XI

Temp. °K.	k for gas phase Q = 24,700		k in CCl_4 solution Q = 25,510	
	Exp't	Calc.	Exp't	Calc.
328	.00150	.00865	.00212	.00258
318	.000498	.00264	.000611	.000753
308	.000135	.000740	.000162	.000203
298	.0000338	.000183	.0000409	.00004978

The results are shown in Table XI and Figure 7. The values of Q were calculated from the temperature coefficient of the reaction velocity by the aid of the Marcelin-Rice equation. Substituting in the Dushman relation, the values of k were found for four temperatures and compared with the values

Fig. 7


Gas Phase
Carbon Tetrachloride
Dushman's Equation
.00300
.00310
.00320
.00330
.00340
.00350
.00360
.00370
Log K
-3
.8
.6
.4
.2
-4
.8
.6
.4
.2
-5
.8
.6
.4
.2
-6
.8
.6
.4

found experimentally both in the gas phase and in this research.

It will be observed that in the gas phase the experimental values are about 500% lower than the calculated values although the differences are not uniform as shown by a comparison of curves 1 and 3 in Figure 7 where the logarithm of the reaction velocity is plotted against the reciprocal of the absolute temperatures as ordinates. On the other hand a far better agreement exists for the decomposition in carbon tetrachloride solution. Furthermore the differences are uniform throughout.

As previously pointed out, the presence of comparatively large amounts of oxygen in direct contact with the nitrogen peroxide in the gas phase system has apparently altered results. This undoubtedly accounts for the incongruity apparent between the experimental and calculated values of k. Although the experimental data in this research does not agree exactly with the calculated values of k, it must be borne in mind that the value of Q, from which those of k have been calculated, is a numerical average of a series of values obtained over small intervals of temperature and none of which lie exactly on the best straight line drawn through them. See Figure 7, Curve 2. A small increase in

the value of Q would make the agreement exceptional and it is hoped that a further series of similar values will show the validity of the Dushman relation.

Summary

1. The decomposition of nitrogen pentoxide in carbon tetrachloride solution is a monomolecular reaction which takes place at room temperature. Such a system is peculiarly applicable to the study of the radiation theory of catalysis and for the radiation hypothesis in general.

2. The rate of decomposition of nitrogen pentoxide was studied between 25° and 55°. The reaction was followed gasometrically by measuring the volume of oxygen liberated.

3. Experiments carried out in the presence of glass wool indicate that the reaction is not catalyzed by the glass walls of the containing vessel. The large temperature coefficient of the reaction shows that the results are not dependent upon diffusion within the solution.

4. The rate of decomposition of nitrogen pentoxide in carbon tetrachloride solution has been shown not to differ from that in the gas phase, to any marked extent.

5. The effect of shaking the decomposition chamber on the value of the velocity constants has been demonstrated. Experiments performed without shaking indicate that a counter-reaction between the nitrogen peroxide and oxygen formed has produced the sub-normal results obtained in a previous study

of the decomposition of nitrogen pentoxide in the gas phase.

6. The critical increment has been shown to be independent of the temperature.

7. The Perrin-Lewis radiation hypothesis requires that the temperature coefficient of the reaction velocity decrease with increased speed of reaction. The data obtained is in agreement with this.

8. The experimental facts indicate the validity of the Dushman theory for unimolecular reactions.

9. Preliminary experiments with chloroform and heptane as solvents show that the reaction velocity is considerably influenced by the medium in which the decomposition takes place.

10. Experiments are in progress with a number of different solvents, chemically unchanged by the nitrogen pentoxide. Attempts will be made to discover a relationship between the reaction velocity and the absorption spectrum of the solvent.

Approved Farrington Daniels.
J. G. Mathews.

Date May 31.

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